# SECONDARY SULPHATES AND CHERT IN THE NULLAGINE SERIES.

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## 1.—The Nullagine Series.

The series of rocks which constitute the Nullagine Formation of A. Gibb Maitland is one of the most important groups of rocks in the whole State of Western Australia, covering as it does not less than 60,000 square miles of country in the north-western part of the State, and reaching a thickness of at least 1,500 feet. This formation consists mainly of horizontal or slightly dipping shales and sandstones with subordinate dolomites and normal limestones. At various points round the eastern and south-eastern edge conglomerates have been observed, whilst towards the northern boundary coarse conglomerates and interbedded lavas and tuffs are developed extensively. Throughout the area covered by the series there are frequent dykes and sills of dolerite, whilst on hill tops cherts and ferruginous laterites are notable features. The beds form in part an immense plateau (peneplain), the remnants of which constitute the Chichester, Hamersley-Ophthalmia, Lofty, Collier and Barlee-Capricorn-Waldberg Ranges, and the highest point in which is Mt. Bruce with an elevation of 4,000 feet. The broad flat valleys formed by the advanced dissection and deflation of this plateau are also, according to H. W. B. Talbot, almost all occupied by Nullagine beds as, except round the extreme borders of the formation, erosion has not reached to the base of the series, and as yet there is no evidence of later sediments of any appreciable extent having been deposited in them, except possibly in the upper Fortescue Valley.

The geological age of the Nullagine beds has not yet been fixed with certainty. No fossils have been found in them, though many of the shale beds are more or less highly carbonaceous, some being in fact quite black in colour, indicating the contemporaneous existence of living organisms. Furthermore, thin limestone beds and concretions of both calcite and marcasite are widespread, and in the genesis of these living organisms often play an important part.

Our estimate of the age of the formation has therefore been based upon evidence other than palæontological, viz.:—

(a.) Structural relationship to other large formations.
(b.) Nature of pebbles included in the conglomerate beds.
(c.) Nature of igneous intrusions.
(d.) Presence of metalliferous veins.
(e.) Extent of structural and chemical change.

The Archæozoic system is represented in the North-West by the Warrawoona igneous schists referable to the Keewatin; and by the Strelley, Minilya, and Murchison granites, referable to the Laurentian. Overlying these unconformably are the Mosquito Creek-Ashburton series of meta-sediments—phyllites, psammites and siliceous conglomerates—the latter, in the Pilbara Goldfield, made up largely of pebbles of Warrawoona jasper. This series is referable to the Huronian. The Nullagine series overlies all three other series, and shows at most points of contact a marked unconformity with the Mosquito Creek beds. The conglomerates of the Nullagine series near Nullagine itself have been found to enclose boulders of Mosquito Creek phyllite and jasper conglomerate, of Warrawoona greenstone schists, of Strelley River granite, and of various intrusive rocks. In regard to the upper limits of the formation, H. W. B. Talbot considers that on the east side in the vicinity of the Paterson and Broadhurst Ranges there is evidence of the Nullagine beds being overlaid unconformably by the South Kimberley Carboniferous.

There is no evidence of the Nullagines being intruded by the pegmatites, acid porphyries or peridotites which are so abundant in the Warrawoona series. On the other hand, intrusive dykes and sills of quartz dolerite are common throughout the series, though they are not known to traverse the Carboniferous anywhere in this region.

Veins of quartz are rare and always small in the Nullagines, though abundant and sometimes of immense size in the three underlying series. Furthermore, whilst the Warrawoona and Mosquito Creek-Ashburton rocks are highly metalliferous, with numerous workable lodes of gold, silver, copper and lead, the Nullagine beds are notoriously poor in these metals. No lead or silver has been recorded from them, and primary gold has been found in only four places, viz., Nullagine, Sunday Hill, Rooney's Patch, and Just in Time. In all four cases the gold occurs in the basal beds of the Nullagine close to auriferous areas of Mosquito Creek or Warrawoona rocks. Copper, which is widespread in the Warrawoona and Mosquito Creek Series, has been found only in small quantities in the Nullagines and at few localities, the only areas of any commercial importance being Kumerina and Ilgarere.

Over immense areas the Nullagine beds are still horizontal or dip at angles less than 25 degrees. Locally, however, A. Gibb Maitland and H. W. B. Talbot have noted sharp folds with dips up to 70°. Of deep seated chemical change there is no evidence, such typical metamorphic minerals as andalusite, garnet, tourmaline, staurolite, etc., being totally absent. The kaolin of the shales has certainly in part been sericitised, but nowhere to the extent of giving the rock the appearance of a mica schist. This micacisation can take place, and in this case has undoubtedly taken place, at no great depth and without any unusual increase of pressure or temperature.

To summarise: our present knowledge indicates that the Nullagine beds are post-Huronian and pre-Carboniferous, and are later that the main metallogenetic epoch in Western Australia. Further, they are not greatly metamorphosed structurally and chemically, and belong to an age in which advanced living organisms were not abundant. The evidence available points to their being of Keeweenawan, Cambrian, or Ordovician Age, probably the first named, though Talbot prefers to correlate them with the Ordovician of South Australia.*

## II.—Nature and Distribution of Sulphates.

The occurrence of secondary sulphates in Nullagine sediments was first brought under the author's notice by specimens of pickeringite and copiapite sent by a prospector from Glen Ross on the Upper Ashburton River. Later the author detected jarosite in several specimens of the auriferous conglomerate from Nullagine, and at various times and localities members of the Geological Field Staff noted gypsum in the Nullagine series. The widespread distribution of such minerals in this formation was, however, first forcibly impressed upon the author during a flying trip made in 1921 with Sir Edgeworth David from Meekatharra to Marble Bar. On this journey the main Nullagine area was traversed completely from north to south, and two days were spent at the type locality. In addition to observing gypsum and epsomite in several places, alunite was detected for the first time in the series in a gully (Alunite Gully) in the Chichester Range between Roy Hill and Bonnie Downs Stations, and with it jarosite. Since then alunite and jarosite have been found at Millstream Station, 200 miles further west in the Fortescue Valley. Finally an efflorescence, consisting of a mixture of pickeringite and tamarugite, sent in recently by a prospector from the Upper Gascoyne is doubtless derived from the Nullagine beds, which cover most of the country in that area.

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* G. S. W. A. Bull. 83, p. 150.

The complete list of secondary sulphates noted is:—

*Normal Sulphates*—

Gypsum, $CaSO_4.2H_2O$.

Epsomite, $MgSO_4.7H_2O$.

Tamarugite, $Na_2Al_2(SO_4)_4.12H_2O$.

Pickeringite, $MgAl_2(SO_4)_4.22H_2O$.

*Basic Sulphates*—

Copiapite, $Fe_4O(SO_4)_5.18H_2O$.

Alunite, $KAl_3O_3(SO_4)_2.3H_2O$.

Jarosite, $KFe_3O_3(SO_4)_2.3H_2O$.

## III. NATURE AND DISTRIBUTION OF THE CHERT.

H. W. B. Talbot writes[*] of the eastern section of the Nullagine region:

".  .  .  .  . The upper stratum on the tops and on the slopes of the ranges and hills composed of sedimentary rocks is indurated by the deposition of silica brought upwards in solution by capillarity, and, owing to the hard and brittle nature of this rock, it is highly susceptible to induration."

Talbot refers[†] frequently to the indurated cherty capping to the Collier and Lofty Ranges, and to the presence at times of a similar induration of the slopes of the ridges. On the other hand, in the Hamersley-Ophthalmia Ranges "the indurated capping is everywhere ferruginous, and there is a marked absence of the silicification of the faces of cliffs, so common in the gorges of other plateaus."[‡] In the ridges about Deadman's Hill, between the Lofty and Ophthalmia Ranges Talbot notes the prevalence of "jaspers" (banded ferruginous cherts) forming part of the Nullagine Series. The low "Chalcedony hills," found at intervals on the Upper Fortescue Plain, are possibly identical formations,[§] but other jasperoid rocks in the Hamersley-Ophthalmia Ranges, are associated with intrusive rocks, and are evidently of the nature of porcellanites. Much further to the east Talbot describes a brecciated chert forming a surface layer of considerable extent above the junction of the Oakover and Davis Rivers.[||]

Talbot describes the cherts mainly *in situ* on the tops or slopes of ridges, but the writer's attention was first drawn to their wide distribution by the frequent "gibber plains," thickly strewn with angular "gibbers," *i.e.*, pebbles and boulders, of chert which occur to the north of the triple junction of the Upper Gascoyne River.

* G. S. W. A. Bull. 83, p. 21.    † Idem pp. 42–46.    ‡ Idem p. 47.
§ Idem p. 98.    || Idem p. 111.

A typical example may be seen at Batthewmurnana Hill, a high butte of Nullagine sediments capped with a 10 to 15 foot crust of chert, boulders of which are thickly strewn on the steep slopes of the butte and on the plain round its base. It is evident that this detrital chert is the result of the lateral erosion of the butte, wind and water having scattered abroad all the softer granules of the shales and sandstones underlying the chert cap.

Twenty miles to the northeast, at Kumerina, the low undulating foot hills of the Collier Range are thickly strewn with chert "gibbers," and are underlain in at least one place (Mineral Lease 37) by gypseous shales.

In the gorges, on the south face of the Chichester Range, a little north of Roy Hill Homestead, the tops of all the spurs are composed of a thick bed of chert, below which, in "Alunite Gully," alunite, jarosite, epsomite, and gypsum are somewhat abundant. At Millstream, shale partly altered to chert has been found close to oxidised pyrite nodules and jarosite veins.

Near Stock Route Well, No. 49, on a plateau below the crest of the Chichester Range, areas of chert are again seen on the surface.

Numerous other localities might be cited, but the examples given illustrate the wide distribution of this chert; its constant occurrence *in situ* as a ridge or plateau capping, or more rarely as a coating on the slopes of ridges of Nullagine sediments; its frequent appearance as angular boulders in the talus slopes and spread over the plains; and its definite association in several places with secondary sulphates.

This chert in hand specimens is a very dense, microgranular rock, containing over 90 per cent. of silica, banded more or less perfectly in structure, and with banded or mottled colouring, varying from dull yellow, through shades of brown to black. Microscopically, it is found to consist mainly of chalcedony, with a little vitreous quartz, mica, and a carbonate in isolated granules. No trace of siliceous organisms has been detected in any of the thin slices. In mass in the ridge cappings the rock is usually distinctly cavernous, dense rock alternating with roughly lenticular cavities of all sizes.

Chert has also been found in Alunite Gully as a complete replacement of calcareous concretions in shale, and, in intimate admixture with limonite, as a replacement of rounded marcasite-pyrite nodules.

### IV.—SOURCE OF THE SULPHATES.

The immense quantities of gypsum found throughout the physiographic province known as the Dry Lake Area, have been considered

by the writer to be due to the evaporation of cut-off areas of a Tertiary ocean retreating to the south or south-east. This ocean appears to have covered an area, roughly, extending between the present south coast and lat. 28°S., and between longs. 117° and 130°E., the exact shoreline at the time of maximum invasion being, of course, quite irregular. One of the strongest arguments in favour of this origin, apart from the discovery of Miocene sponges on both sides of the Stirling Range and as far inland as the extreme north end of Lake Cowan, is the close association of the gypsum deposits with salinas, the subsurface water of which closely resembles an evaporated ocean water. Three examples of this will suffice:—

*Subsurface Water from Salinas, Dry Lake Region.*

| | Lake Monger, Wubin Downs. | Lake Goongarrie,* Comet Vale. | Lake Cowan, Norseman. |
|---|---|---|---|
| | % | % | % |
| CaCO$_3$ ... ... ... | ·004 | ·002 | ·008 |
| CaSO$_4$ ... ... ... | ·136 | ·133 | ·224 |
| MgSO$_4$ ... ... ... | 2·765 | 2·153 | 1·132 |
| MgCl$_2$ ... ... ... | 4·374 | 2·994 | 3·190 |
| KCl ... ... ... ... | ·970 | ·038 | ·074 |
| NaCl ... ... ... | 24·251 | 20·107 | 18·881 |
| NaBr ... ... ... | ·023 | *Nil* | not det. |
| NaNO$_3$ ... ... ... | *Nil* | *Nil* | *Nil* |
| SiO$_2$, Al$_2$O$_3$, etc. ... ... | ·005 | ·030 | ·004 |
| | 32·528 | 25·457 | 23·513 |

* From shaft half mile from lake.

The overwhelming proportion in these waters of common salt and the large amounts of magnesium sulphate and chloride, all typical cyclic salts, point to their being beyond all doubt ocean residuals. Further it is to be noted that all the well waters throughout this area give evidence of this absorption of ocean water by the weathered rocks below a fairly definite contour line ranging between 1,000 and 1,500 feet above present ocean level.

No similar evidence is presented by the dry area* covered by the Nullagine series in the North-West Division of the State. Subsurface and surface waters even in low-lying and arid areas are for the most part fresh or only brackish, and in the latter case

* Most of this region has a rainfall under 10 inches per annum.

the constituent solids do not point to any direct relationship with ocean water. Typical examples of these waters are:

*Subsurface Water from Nullagine Region.*

| — | Town Well, Nullagine. | Homestead Well, Ethel Creek. | S.R. Well 41, Mundi-windi. | Copper Mine, Kumerina. |
|---|---|---|---|---|
| | % | % | % | % |
| $FeCO_3$ ... ... | ·0002 | trace | trace | trace |
| $CaCO_3$ ... ... | ·0171 | ·0142 | ·0155 | ·0202 |
| $MgCO_3$ ... ... | ·0305 | ·0329 | ·0080 | ·0105 |
| $Na_2CO_3$ ... ... | ... | ·0099 | ... | ... |
| $CaSO_4$ ... ... | ... | ... | ... | ... |
| $MgSO_4$ ... ... | ·0633 | ... | ·0144 | ·0307 |
| $Na_2SO_4$ ... ... | ·0708 | ... | ... | ... |
| $K_2SO_4$ ... ... | ·0227 | ·0036 | ·0031 | ·0042 |
| $KNO_3$ ... ... | ... | ·0139 | ... | ... |
| $NaNO_3$ ... ... | not det. | ... | ·0055 | trace |
| $MgCl_2$ ... ... | ... | ... | ... | ... |
| $KCl$ ... ... | not det. | ·0101 | ·0040 | ·0006 |
| $NaCl$ ... ... | ·1700 | ·0025 | ·0334 | ·0337 |
| $SiO_2$ ... ... | ·0025 | ·0064 | ·0050 | ·0014 |
| $Al_2O_3$ ... ... | ·0009 | ·0008 | ·0004 | ·0008 |
| Total solids ... | 0·3780 | 0·0943 | 0·0893 | 0·1021* |

* Also trace of copper carbonate.

The Nullagine sediments were probably marine, but they are so ancient and so well dissected and drained that the greater part of the originally associated ocean water might well be expected to be washed out of them. The absence of potential $CaSO_4$ and $MgCl_2$ from the tabulated waters, and the low content in $NaCl$ of nearly all of them show that they are not of the marine type. Further the presence of alkali sulphates in minerals found in the Nullagine rocks, and of potential alkali sulphates in the waters indicates a predominance of the sulphate ion never found in ocean waters. Finally, certain of the sulphates now found in the sediments have never been recorded as constituents of marine salt beds such as those of Alsace or Germany. The compounds referred to are the alums, tamarugite and pickeringite, and the basic sulphates, alunite and jarosite.

After due consideration of all the circumstances of their occurrence the conclusion is reached that, in the absence of any indication of fumarole action, the sulphates must originate in the oxidation of marcasite and pyrite occurring in the sediments, and to a lesser extent in the associated lavas. Small quantities of pyrite are a primary product of consolidation of the lavas which are widespread in the Chichester Ranges, and further north. In some places these have suffered considerable oxidation, but as a rule they are very dense and fresh. At Nullagine, Kumerina, and

possibly at a few other points metalliferous veins in the Nullagine Series carry pyrite and other sulphides. These give rise to sulphates in the immediate vicinity but only account for a minor portion of the whole. On the other hand concretions of marcasite and pyrite are found at many points embedded in carbonaceous shales, and over a wide area pseudomorphs of limonite after these sulphides have been found in situ in the shales and loose in the talus slopes and creek beds.

For many years past specimens have reached Perth from the North-West consisting of limonite (micogranular goethite) pseudomorphs after cubes and round concretions of iron sulphide. These have now been seen *in situ* in several localities, and unaltered and partly altered concretions of sulphide have been collected at Millstream Station and elsewhere.

The sulphide concretions from all parts of the region bear a very close resemblance to one another. They are mostly spherical in outline but not uncommonly ovoid or lenticular, and occasionally have a form suggesting the coalescence of several concretions which have grown from nuclei lying a little distance apart from one another. They vary in diameter from about 1 to 7 cm. (0·5 to 3·0 inches), and have a rather rough surface made up of small cube or octahedron faces. That they usually consist of three fairly distinct layers is evident even in fresh specimens, but is much more apparent in those which are partly or wholly altered to goethite (see fig. 1). The centre is a massive iron sulphide, which may be either marcasite or pyrite. It frequently contains a few granules or minute crystals of quartz and weathers to a porous mass which drops out when an oxidised concretion is split open. Encrusting this core is a thick layer of radially prismatic marcasite, which usually forms by far the major portion of the whole nodule. The surface is composed of a thin continuous crust of pyrite crystallised in cubes, or rarely octahedra (see fig. 1).

The matrices of these concretions are grey or black carbonaceous shales, possibly occurring at more than one horizon in any given section. One of the localities at which entirely unaltered concretions have been exposed by rapid lateral erosion, is Millstream Station on the Lower Fortescue, about one mile north-west of the homestead. There the matrix is a jet black thinly laminated shale. This locality has yielded the largest nodule yet seen, viz., 7 cm. in diameter with an attached satellite 3 cm. in diameter. The marcasite of this particular nodule was partly oxidised, and the surface pyrite showed numerous octahedron faces. Precisely similar sulphide nodules are known to occur at Tambrey Station about 30 miles east of Millstream, and A. Gibb Maitland has noted[*] that pyrite is abundant in shales at Broad Flat Well between Millstream and Tambrey.

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[*] G.S.W.A. Bull. 33, p. 122.

A rough shapeless nodule with dense interior and pyrite faces on the surface has been collected at Mt. Florence Station, 20 miles further to the south-east. This may be composed wholly of pyrite. At Bulla Downs Station, south of the Ophthalmia Range, there are numerous small concretions in a grey shale. These are either subspherical or lenticular in form, and are composed of marcasite and pyrite like those found farther to the north-west.
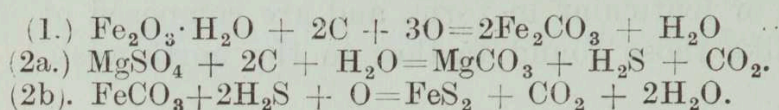
Fig. 1.
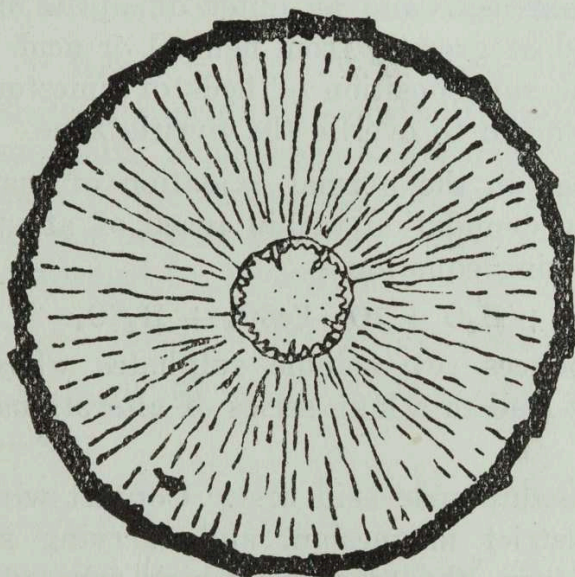


Goethite Pseudomorph after Marcasite-Pyrite
Concretion, Millstream Station.

The progress of erosion over most of this region is much more rapid laterally than vertically under recently existing conditions. Even laterally it is usually slower than the progress of subsurface oxidation, for which reason unoxidised concretions of iron sulphides are much less in evidence than are goethite pseudomorphs after them. Such pseudomorphs are reported to be especially plentiful on the West Pilbara Tableland, north of the Lower Fortescue. Here, and in many other localities, they are found still embedded in the Nullagine shales, or lying loose in stream beds or on the slopes of the deep gorges which penetrate the Nullagine peneplain. Other typical localities are Just-in-Time, west of Marble Bar; Millstream and Tambrey Stations on the southern scarp of the West Pilbara Tableland; Alunite Gully at the east end of the Chichester Range; and Balfour Downs Station near the head of the Oakover River.

V.—CHEMISTRY OF THE ORIGIN AND ALTERATION OF THE SULPHIDES.

Pyrite and marcasite are quite common constituents of carbonaceous sediments of all ages. They are usually ascribed to the re-

duction of the water soluble sulphates to sulphides by inorganic or organic (bacterial) action, and the interaction of these sulphides with ferrous carbonate, which is always present when carbonaceous matter and ferric hydroxide come into contact. The reactions may be represented thus:—

(1.) $Fe_2O_3 \cdot H_2O + 2C + 3O = 2Fe_2CO_3 + H_2O$

(2a.) $MgSO_4 + 2C + H_2O = MgCO_3 + H_2S + CO_2$.

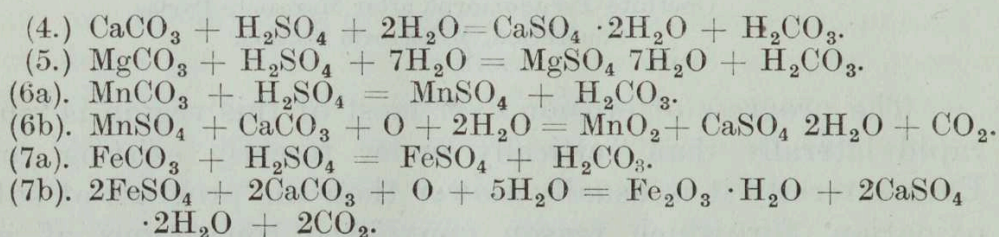(2b). $FeCO_3 + 2H_2S + O = FeS_2 + CO_2 + 2H_2O$.

Marcasite is the principal sulphide formed when the medium is acid or neutral in reaction, pyrite when it is alkaline. Nodules with an inner layer of marcasite and an outer of pyrite indicate a change, during the period of growth, from neutral or acid to alkaline conditions, e.g., by the superposition of beds of limestone, which, in several places are known to overlie the pyritic zone.

The first step in the normal oxidation of marcasite or pyrite, when brought by denudation within reach of atmospheric influence, follows the following equation:—

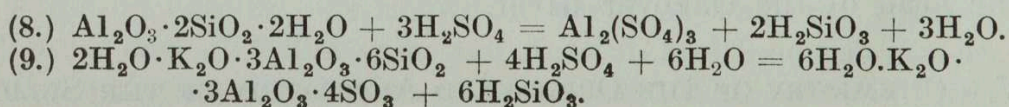(3.) $FeS_2 + H_2O + 7O = FeSO_4 + H_2SO_4$.
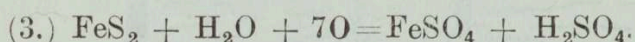
This action produces two soluble sulphates whose migration and chemical activity lead to a long series of alterations in the associated sediments.

To trace the sulphuric acid first. Contact with a limestone, always in this district magnesian, and carrying small amounts of manganese and iron, the reactions which take place quite rapidly are—

(4.) $CaCO_3 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + H_2CO_3$.

(5.) $MgCO_3 + H_2SO_4 + 7H_2O = MgSO_4 \ 7H_2O + H_2CO_3$.

(6a). $MnCO_3 + H_2SO_4 = MnSO_4 + H_2CO_3$.

(6b). $MnSO_4 + CaCO_3 + O + 2H_2O = MnO_2 + CaSO_4 \ 2H_2O + CO_2$.

(7a). $FeCO_3 + H_2SO_4 = FeSO_4 + H_2CO_3$.

(7b). $2FeSO_4 + 2CaCO_3 + O + 5H_2O = Fe_2O_3 \cdot H_2O + 2CaSO_4 \cdot 2H_2O + 2CO_2$.

These equations indicate the final products of the action of sulphuric acid upon limestone to be gypsum, epsomite, pyrolusite, and goethite. At Alunite Gully (vide infra) such a series of minerals is actually associated with goethite pseudomorphs after iron sulphide modules, and chert pseudomorphs after calcite.

The action of the acid upon the shales immediately in contact with the nodules is equally interesting. These shales consist largely of muscovite, kaolin, and quartz. The last is unaffected by acid, but the other two are slowly attacked according to the following scheme:—

(8.) $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 2H_2SiO_3 + 3H_2O$.

(9.) $2H_2O \cdot K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 + 4H_2SO_4 + 6H_2O = 6H_2O.K_2O \cdot 3Al_2O_3 \cdot 4SO_3 + 6H_2SiO_3$.

Equation (8) shows the formation from kaolin of solutions of aluminium sulphate, which in the presence of alkali or magnesium sul-

phates in the ground waters, would yield alums so long as the solutions are notably acid, and alunite or natroalunite, if they became only faintly acid or neutral. Were the solutions to come in contact with limestone, gibbsite would result, minerals of the alum and alunite series being unstable in the presence of even weak alkalis. Equation (9) shows the direct derivation of alunite from sericite.

The ferrous sulphate solution formed in the original oxidation of the marcasite or pyrite (equation 3) may, early in its career, be precipitated by limestone to form goethite according to equation (7b). In the absence of limestone, and the solution remaining acid, oxidation to ferric sulphate would be observed, thus:—

(10.) $2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$
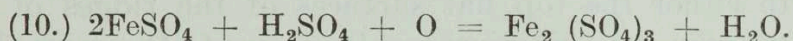
This oxidation reduces the acidity to one-half, and favours the tendency to form basic salts, a tendency still further increased by the neutralisation of part of the remaining acid by kaolin, etc. So long as the solution does not become alkaline there is a strong probability of copiapite being formed by hydrolysis:—

(11.) $2Fe_2(SO_4)_3 + 19H_2O = 2Fe_2O_3 \cdot 5SO \cdot _3 18H_2O + H_2SO_4.$
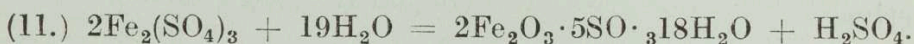
In the presence of alkalis in the ground water, jarosite or matrojarosite would result:—

(12.) $3Fe_2(SO_4)_3 + (K,Na)_2 SO_4 + 12H_2O = 6H_2O. \; (K,Na)_2O.$
$3Fe_2O_3 \cdot 4SO_3 + 6H_2SO_4.$
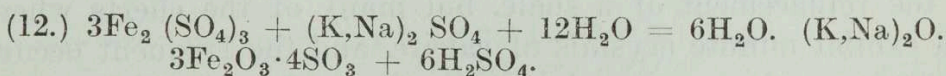
We have thus accounted for the derivation of all the observed sulphates.

Equations (8) and (9) show the formation of soluble silicic acids during the oxidation of the pyrite nodules. This is of the greatest significance when considered in the light of the wide distribution of chert as a surface formation, not only the ridge and mesa tops but also on the slopes of the rises, as described by Talbot.

Attempts have been made from time to time to account for such cherts as the result of—

(1) Consolidation *in situ* of beds of opal of organic origin, viz., the skeletal remains of sponges, radiolaria, or diatoms.

(2) Formation by lateritic action from solutions of silica produced by the action of ground water of normal composition on underlying quartz grains.

So far as the Nullagine cherts are concerned, sections of specimens of these rocks collected by both H. W. B. Talbot and the present writer, and examined by R. A. Farquharson, have shown no trace of organic structure, and, furthermore, the chert beds appear on the present surface of the ground no matter what horizon it represents, and have not been recognised interbedded below the tops of the ridges. Again, they have been found by Talbot as a thin

sloping coat on the shale outcrops, with which they are unconformable.*

With regard to the second explanation given above, the solubility of quartz in ground waters at the normal temperature and pressure is so minute that this explanation fails utterly to account for the accumulation of several feet, in places as much as 12 feet, or more, or chert capping. On the other hand the silicic acid generated in accordance with equations (8) and (9) from the action of weathering sulphides upon kaolin and mica, would be sufficient to provide the material for the chert beds, and would be generated in a form and under circumstances especially favourable to its transport by capillarity to either the top flat surfaces of the ridges or their exposed sloping outcrops. Erosion would prevent its accumulation in large masses on the latter. In this connection it is to be noted that the attack of the shales by the sulphuric acid solution may take place wholly in the beds where the sulphides are decomposing, or in part at the surface, whither the acid solutions may migrate, and where they will become concentrated by evaporation, and therefore more active.

Whether an original bed of limestone had any part in the formation of the chert is not certain, their thinly bedded structure suggests the replacement of a shale, but many of the cherts when sectioned exhibit minute crystals of calcite, and the frequent occurrence of chert or opal as a pseudomorph after calcite has been noted in every region of the world. At Alunite Gully chert pseudomorphs after calcite concretions are quite abundant. No explanation of this phenomenon appears to have been put forward, but it is probably due to the formation of a solid hydrous calcium silicate by interaction between limestone and silicic acid solutions, and the subsequent decomposition of the silicate by atmospheric carbonic acid. This indicates a reaction of the following type which is reversible under slight variations of conditions—

$$H_2SiO_3 + CaCO_3 = CaSiO_3 \cdot H_2O + CO_2.$$
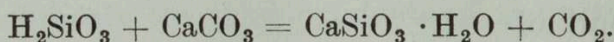
the silicic acid ultimately becoming fixed at the exposed surface by dehydration in the hot sun and dry air.

## VI.—Locality Notes.

*Alunite Gully*, Chichester Range, (Roy Hill Station).— Alunite was first found by the writer a few yards upstream from the point where the Roy Hill-Nullagine motor road and telegraph line cross the creek. This is about nine miles south-east of Well 48. Attention was called to the locality by the numerous boulders of manganese ore in the stream bed. The sides of the gully are steep slopes of almost horizontally bedded Nullagine shales and soft sandstones with a prominent chert capping 10ft. thick. The total height

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* G.S.W.A. Bull. 83, pp. 42–45, etc.

of the cliffs is from 70 to 100 feet. Most of the pebbles in the stream are chert or flint, but manganese ores are abundant for some distance along the stream below the point where alunite and manganese ore were found *in situ*, on opposite sides of the gully. Limonite pseudomorphs after pyrite-marcasite nodules are not uncommon in the talus and creek bed.

A section through the alunite site is shown in Figure 2. Below the chert cap the whole section consists of thinly bedded shales and soft sandstones. About half way down, a powdery shale carries innumerable crystals of gypsum averaging about 25 mm. (1 inch) in length. In close association are found numerous chalcedony "buns"

Fig. 2.
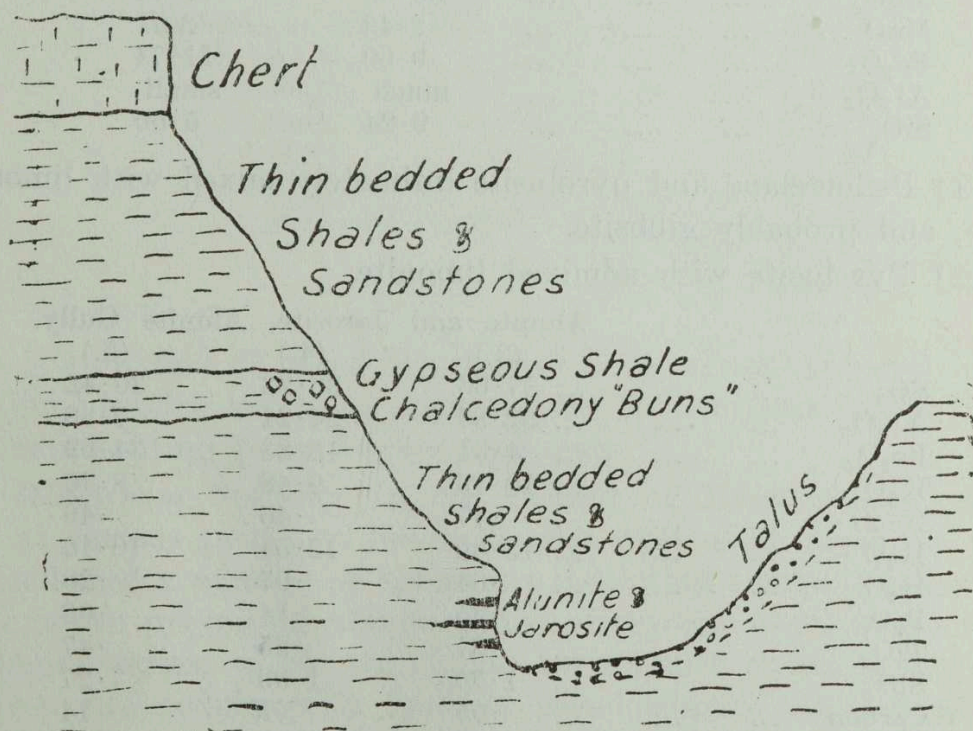


Section at Alunite Gully, Chichester Range.

or flinty replacements of calcareous concretions, ranging from 3 to 15 cm. in diameter. In the bottom six feet of the section, where the stream has cut a vertical face in soft carbonaceous shales, numerous thin lenses of yellowish-white to ochre-yellow alunite are interbedded with the shales. These lenses are from 2.5 to 5 cm. (1 to 2 in.) in thickness. The mineral in them is granular and porous like the Kanowna alunite, and whilst occasionally very friable, is more often moderately tough. The frequent yellow colour is due to intergrown jarosite, comparatively pure specimens of which are found in associated flat cakes as thick as the alunite lenses, but much less extended and inclined to be mammilated in outline. Fairly pure jarosite also forms borders to some of the alunite lenses. A few yards farther downstream a white fibrous efflorescence was abundant in a sheltered

part of the creek bank. This proved to be epsomite, with traces of salt, but no gypsum or alum. On the opposite side of the narrow gully the shale at the gypsum horizon showed no gypsum but instead was strongly impregnated with hydrated iron and manganese ores, the latter also forming veinlets and flat interbedded cakes with mammilated surface. This was proved to be the source of the boulders of psilomelane and pyrolusite in the creek bed. The paragenesis of the various secondary minerals found here has been dealt with on a previous page.

Analyses have been made of several of the minerals, the results being as follow:—

| | | | | Manganese ores, Alunite Gully. | |
| --- | --- | --- | --- | --- | --- |
| | | | | (1.) | (2.) |
| | | | | Amorphous. | Crystallised. |
| $MnO_2$ | ... | ... | ... | 60·66 | 77·74 |
| $MnO$ | ... | ... | ... | 2·43 | $Nil$ |
| $Fe_2O_3$ | ... | ... | ... | 9·60 | 11·74 |
| $Al_2O_3$ | ... | ... | ... | much | small |
| $SiO_2$ | ... | ... | ... | 9·24 | 5·60 |

(1) Psilomelane and pyrolusite intimately mixed with limonite, kaolin, and probably gibbsite.

(2) Pyrolusite with admixed limonite.

| | | | Alunite and Jarosite, Alunite Gully. | | |
| --- | --- | --- | --- | --- | --- |
| | | | (3.) | (4.) | (5.) |
| $SO_3$ | ... | ... | 37·66 | 36·23 | 30·42 |
| $Al_2O_3$ | ... | ... | 32·87 | 24·21 | 7·88 |
| $Fe_2O_3$ | ... | ... | 4·01 | 15·83 | 34·69 |
| $K_2O$ | ... | ... | 10·19 | 9·48 | 8·46 |
| $Na_2O$ | ... | ... | ·47 | ·46 | ·46 |
| $H_2O+$ | ... | ... | 13·09 | 12·54 | 10·16 |
| $H_2O-$ | ... | ... | ·04 | ·07 | ·20 |
| $P_2O_5$ | ... | ... | ·25 | ·14 | ·06 |
| $TiO_2$ | ... | ... | ·31 | ·25 | ·47 |
| $SiO_2$ | ... | ... | 1·30 | 1·09 | 7·27 |
| Carbon | ... | ... | ·05 | $Nil$ | ·14 |
| NaCl | ... | ... | trace | ·13 | $Nil$ |
| | | | 100·24 | 100·43 | 100·21 |

Equal to

| | | | | | |
| --- | --- | --- | --- | --- | --- |
| Jarosite | ... | ... | ... | 8·4 | 32·9 | 72·4 |
| Alunite | ... | ... | ... | 89·4 | 65·6 | 18·8 |
| Quartz | ... | ... | ... | 1·3 | 1·1 | 7·3 |

(3) Almost pure white, friable, porous alunite from 2.5 cm. vein. Under microscope it is all perfectly crystallised in pseudocubes 3 to 7 microns in diameter. Faces present $r^1r^2r^8r_1r_2r_3$.

(4) Naples yellow (Ridgway 19¹e), tough, porous alunite from 4 cm. vein. Fairly well crystallised in pseudo-cubes of 3 to 5 microns.

(5) Jarosite cake with banded colouring, mustard yellow (19¹b) to citrine drab (21¹¹¹i), due to irregular distribution of alunite and carbonaceous matter. Porous and microgranular.

*Chert, Alunite Gully.*

(6).  $SiO_2$  $Al_2O_3$  $Fe_2O_3$  $CaCO_3$  $H_2O+$  Total
97·60  *Nil*  1·95  0·21  0·25  100·01

(7) Banded brown chert from summit of ridge.

*Conical Hill, Lofty Range.*—Five miles north-east of Conical Hill at the western end of Lofty Range, H. W. B. Talbot found the Nullagine shales to enclose numerous concretions of calcite. These were oblate spheroids or ellipsoids, and represent the type of concretion which gave rise to the chalcedony "buns" of Alunite Gully. An analysis was made of one of the Lofty Range concretions, measuring 7.5 x 5.5 x 2.5 cm.

*Calcite Concretion near Conical Hill.*

| | | | | | |
|---|---|---|---|---|---|
| Insoluble in dilute HCl | ... | ... | ... | 25·14 |
| Soluble $Al_2O_3$ | ... | ... | ... | ... | 1·62 |
| $Fe_2O_3$ | ... | ... | ... | ... | 3·66 |
| CaO | ... | ... | ... | ... | 37·72 |
| MgO | ... | ... | ... | ... | 1·26 |
| $CO_2$ | ... | ... | ... | ... | 29·61 |
| $H_2O$ and organic | ... | ... | 1·35 |
| | | | | | 100·36 |

This is a mixture of about two-thirds calcite, one-third kaolin, quartz and limonite, the last being evenly distributed through the concretion and representing prior ferrous carbonate.

*Millstream Station.*—In the vicinity of Millstream homestead, and at various points to the south and west of it, L. A. Le Souef has collected a number of specimens indicating similar conditions to those which prevail at Alunite Gully. Grey and black shales of the Nullagine series, which are almost horizontally bedded, carry marcasite-pyrite nodules with limonite pseudomorphs after them. The pseudomorphs are spherical or lenticular in form, with diameters ranging from 2 to 7 cm. Usually they consist of fairly pure limonite, but at other times of an intimate mixture of chalcedony and limonite. Their surfaces are finely to coarsely crystallised, showing mostly cube faces, though one specimen had octahedron faces only, and others showed both forms. A typical specimen contained:—

| $Fe_2O_3$ | $Mn_2O_3$ | $Al_2O_3$ | $SiO_2$ | $H_2O+$ | $H_2O-$ | Total |
|---|---|---|---|---|---|---|
| 86·61 | 0·22 | 1·69 | 2·07 | 9·02 | 0·18 | 99·79 |

Chert is also found, and one specimen is composed of thin bedded shale, partly altered to chert, the boundaries between the silicified and unsilicified portions being sharply defined, but very irregular.

Jarosite is fairly abundant. Two miles east of Gregory's Gorge it forms a vein 2 to 2.5 cm. wide, cutting across the flat shales at an angle of 60°. The colour is close to mustard yellow (between Ridg-

ways 19¹b and 19¹d). It is highly porous, but tough, and made up of microscopic granules. Only a very few of the grains are recognisable as crystals under the microscope, these being transparent hexagonal plates with dark centres. Its composition is:—

| $SO_3$ | $Fe_2O_3$ | $Al_2O_3$ | $K_2O$ | $Na_2O$ | $H_2O-$ | $H_2O+$ | $P_2O_5$ | $TiO_2$ | $SiO_2$ | C |
|--------|-----------|-----------|--------|---------|---------|---------|----------|---------|---------|---|
| 32·96 | 35·14 | 9·11 | 9·78 | *Nil* | 0·16 | 11·84 | 0·57 | 0·14 | 0·82 | *Nil* |

Total ... ... 100·52

This represents a mixture of

| Jarosite. | Alunite. | Quartz, etc. |
|-----------|----------|--------------|
| 73·5 | 24·6 | 2·0 |

The calculated density of this mixture is 3.06. The actual density of the mass was found to be 3.02, pure jarosite being 3.20.

In Gregory's Gorge, about 15 miles west of the homestead, a similar vein-filling of jarosite was found to carry the following constituents soluble in HCl—

| $K_2O$ | $Na_2O$ | NaCl |
|--------|---------|------|
| 7·87 | 1·32 | 0·29 per cent. |

About 15 miles south of the homestead there is an almost vertical and persistent vein of impure alunite 8 to 10 cm. wide. This is white or yellow in colour with bright red and brown iron stains. It has a columnar to almost fibrous structure across the vein. It is tough but highly porous, and under the microscope is seen to be granular and imperfectly crystallised, the pseudo-cubical crystals being 2 to 5 microns in diameter. Some of the whiter material was found to contain—

| $K_2O$ | $Na_2O$ | $SO_3$ |
|--------|---------|--------|
| 7·77 | 0·36 | 26·42 |

This is equal to about 70 per cent. alunite, the balance being mainly siliceous matter. The yellower portions of the vein contain a little jarosite in intimate admixture.

*Tambrey Station.*—Between Tambrey homestead and Middle Creek police station, limonite pseudomorphs after marcasite-pyrite nodules precisely similar to those found at Millstream are abundant under like geological and physiographical conditions. This locality is worthy of a careful search for alunite and other secondary sulphates.

*Nullagine.*—On the slopes around Watty's Flat, which is the centre of gold mining activity, efflorescences of water-soluble salts are common in dry weather. A very abundant powdery white efflorescence was found on the slopes on the east side of the flat, covering to a depth of several centimetres an outcrop of a bedded white kaolin (kaolinised lava?) of the Nullagine Series. This efflorescence was found to consist of—

| Kaolin. | Gypsum. | Epsomite. | $Na_2SO_4$ | NaCl | Total. |
|---------|---------|-----------|------------|------|--------|
| 71·3 | 17·2 | 10·6 | 0·5 | 1·4 | 100·0 |

A similar looking efflorescence was found just under the hard grit capping of a knoll of Nullagine sediments to the south-west of the last described specimen. This was found to be mainly epsomite, with a little salt, and some kaolin and fine quartz sand.

At the head of Grant's Gully, on the west side of Watty's Flat, a tunnel and winze have been put in to follow a prominent auriferous zone of the Nullagine conglomerate. In the winze the conglomerate is highly pyritous, the sulphide occurring in scattered crystals and granular aggregates as well as in well water-worn pseudomorphs after some highly ferruginous silicate rock (see analysis below). On the walls of the tunnel above the sulphide zone, a pure white efflorescence was collected which consisted chiefly of granular, highly birefringent epsomite, with traces of gypsum, and a little alum (pickeringite ?), the solution containing aluminium sulphate.

Tracing the outcrop of this slightly-dipping auriferous zone round the brow of Bingham's Hill where it has been mined to a short distance at very many points, the gold-bearing rock was found to be characterised throughout by an unusual amount of limonite at the outcrop. A few feet in from the surface the limonite was frequently found to give place to jarosite, the bright yellow mineral forming an excellent guide to the width and direction of the auriferous impregnation.

Typical specimens of sulphide and oxidised conglomerate (G. S. M. *1/1387, 1/1483) were found to have the following composition:—

### Auriferous Conglomerate, Nullagine.

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | FeO | MnO | MgO | CaO | $Na_2O$ |
|---|---|---|---|---|---|---|---|---|
| Sulphide | 54·56 | 4·74 | 0·89 | 0·17 | Nil | 0·38 | 0·32 | 0·52 |
| Oxidised | 60·65 | 5·79 | 20·22 | 2·07 | Nil | 0·44 | Nil | ·64a |

| $K_2O$ | $H_2O-$ | $H_2O+$ | $TiO_2$ | $CO_2$ | $P_2O_5$ | $SO_3$ | $FeS_2$ | Cl | As | Ni |
|---|---|---|---|---|---|---|---|---|---|---|
| 1·32 | 0·20 | 1·87 | 0·19 | Nil | 0·18 | Nil | 34·57* | trace | ·06 | ·02 |
| 1·70a | ·77 | 4·13 | ·11 | Nil | 0·04 | 3 49 | Nil | ·02 | trace | Nil |

| Pb, Cu, Bi, Co, Zn, Sb. | Total | Gold b | Silver b |
|---|---|---|---|
| Nil | 100·01 | 0·500 | 0·350 |
| Nil | 100·07 | 1·144 | 0·162 |

a Sol. in HCl ; $Na_2O$, 0·18 ; $K_2O$, 1·02.      b. Ounces per ton.
* Fe, 16·09 ; S, 18·48.

The oxidised ore is calculated to contain 10.95 per cent. of jarosite of the following composition:—

### Jarosite, Nullagine.

| $SO_3$ | $Fe_2O_3$ | $K_2O$ | $Na_2O$ | $H_2O$ | Total |
|---|---|---|---|---|---|
| 32·2 | 48·1 | 7·5 | 1·3 | 10·9 | 100·0 |

* Register numbers in the Geological Survey collection.

On examination of this and numerous other specimens of a similar nature for jarosite, it was found that many oval or cubical cavities originally known to be occupied by pyrite, were wholly or partly filled with a bright yellow mineral sometimes in soft powder, sometimes in fine dense masses. This mineral gave all the chemical reactions for jarosite, and under the microscope was found to be composed of transparent amber-yellow crystals of the hexagonal system, the faces being $r^1r^2r^8r_1r_2r_3c^1c_1$. The diameter of the crystals varied from 0.005 to 0.100 mm. In addition to the cavity fillings, quite a considerable amount of jarosite was found to be present as strings and masses of small rounded granules, impregnating the kaolinised rock pebbles, and chalcedonic binding material of the conglomerate. (*Vide* G.S.M. 1509, 3167, 1/1483.)

*Glen Ross* (Upper Ashburton River).—In a carbonaceous shale in this locality pickeringite forms a network of veins averaging one centimetre in width. It is colourless and substranslucent, with a compact sub-fibrous structure. An analysis shows:—

*Pickeringite. Glen Ross.*

| $Al_2O_3$ | MgO | MnO | FeO | $K_2O$ | $Na_2O$ | $SO_3$ | $H_2O$ | Total |
|---|---|---|---|---|---|---|---|---|
| 12·01 | 4·15 | 0·60 | trace | 0·08 | *Nil* | 37·28 | 45·93 | 100·05 |

The density of the mineral is 1.87; hardness 2.5; mean refractive index, 1.45. It is readily soluble in water, and effloresces on exposure to dry air. The analysis shows it to be typical pickeringite,

$$MgSO_4 \ Al_2 (SO_4)_3 \cdot 22H_2O.$$
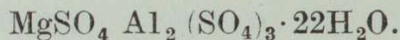
*Upper Gascoyne River.*—A greyish white efflorescence collected somewhere on the Upper Gascoyne in 1921 was found to be a mixture of 35 per cent. clay and sand with 65 per cent. soluble sulphates. An analysis of the latter showed—

| $SO_3$ | $Al_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | Cl | $H_2O$ | Total | Less O = Cl |
|---|---|---|---|---|---|---|---|---|---|
| 45·37 | 12·57 | ·55 | 1·81 | 10·43 | ·03 | 1·39 | 28·16 | 100·31 | 0·31 |

Recrystallisation gave many monoclinic crystals with much fine granular matter.

There is little doubt that the chief constituents of this efflorescence are tamarugite ($Na_2O.Al_2O_3.4SO_3.12H_2O$) and pickeringite (magnesia alum), but as no definite information regarding its occurrence is obtainable, there is some doubt whether it was derived from Nullagine sediments.

## VII.—Summary.

This paper describes the occurrence and genesis of chert and of several secondary sulphates in the Nullagine series of the North-Western Division of Western Australia.

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I. The introduction gives a brief résumé of the present state of knowledge of the Nullagine beds, whose age is tentatively given as Keweenawan.

II. The sulphates recorded are gypsum, epsomite, tamarugite, pickeringite, copiapite, alunite, and jarosite. These are found either as vein fillings, efflorescences or embedded crystals in soft sediments.

III. Chert is shown to be widespread over the Nullagine region as hill cappings or coatings to hill slopes, and as thickly strewn "gibbers" on broad plains.

IV. In tracing the origin of the sulphates differences are indicated between the ground waters of the Dry Lake Region and of the Nullagine region, typical new analyses being given of both. The prevalence in the Nullagine series of pyrite-marcasite concretions and goethite pseudomorphs after them is emphasised.

V. The paragenesis of the sulphates and chert, and of some associated minerals, is detailed, and their origin traced to the weathering of the pyrite and marcasite.

VI. Descriptions of individual occurrences are given, including new analyses of the sulphates, chert, and associated minerals from this region.